AFRL-SR-BL-TR-98-

0610

REPORT DOCUMENTATION PAGE

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	27 August, 1998	Final, June 1, 1995 – August 15, 1998

4. TITLE AND SUBTITLE
Ultrafast Dynamics of Energetic Additives in O_2 Clusters
Supplement for

5. FUNDING NUMBERS
F49620-95-I-0408
3484/ YS
61103D

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10. SPONSORING / MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

Approved for public release

12a. DISTRIBUTION / AVAILABILITY STATEMENT

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 Words)*

Extensive theoretical and experimental studies of the photochemistry of energetic cluster ions and the dynamics of molecular reactions within size-selected clusters have been carried out over the past three years. Photodetachment, photoelectron spectroscopy and photodissociation spectroscopy have been utilized to determine the structure of transient species. Incoherent control of reaction products in a cluster ion containing 35 atoms has been demonstrated and, more importantly, it has been shown that such a large tightly coupled complex can maintain a very non-statistical, chemically significant amount of excitation for at least 10 ps. This result sets the time scale for possible control strategies. A new method has been developed to follow reaction dynamics in real time, starting with negative ion photodetachment to produce in energetic neutral, followed by a multiphoton ionization with a delayed ultrafast probe pulse. Direct information about coherent motion of the solvent itself is obtained by following the absorption recovery as detected by specific two-photon products, since it is the instantaneous cage configurations that determine the product branching ratios at given pump-probe delays.

14. SUBJECT TERMS	15. NUMBER OF PAGES
Cluster Ions, Caging, Incoherent Control, Cluster Additives	
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	

AASERT Final Technical Report

F49620-95-1-0408

SUPPLEMENT
for
Ultrafast Dynamics of Energetic Additives in O_2 Clusters

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27 August, 1998

Objectives:

One goal of this research program were to provide advanced training for graduate students in the areas of molecular dynamics and energetic ionic clusters, focussing on topics of possible Air Force relevance. Another goal was to develop experimental methodologies to determine and possibly control the structure of ionic clusters, as a prelude to developing energetic additives.

Accomplishments:

This brief report summarizes our activities and lists publications over the period of this grant. This AASERT Grant has supported three different Graduate students over the past three years: Maria Nadal, Joseph Kim and Sreela Nandi. They have each worked as a major contributor in our research projects involving cluster ion chemistry, cluster ion-solvent dynamics, transition state spectroscopy, and charge reversal spectroscopy. In the past few months, support has been provided for two new students, Tanya Ramond and Todd Sanford.

Nadal and Nandi have carried out extensive[1-7] studies of the stability of a diatomic ion inside a small cluster as a function of the strength of the cluster itself and of the kinetic energy release upon photodissociation. When the solvent surrounding the ion is a strong binder (CO_2, N_2O or OCS), and the chromophore is I_2^-, the cage fraction is 100% for moderate (0.5 eV) kinetic energy release. When the surrounding solvent is Ar, the cage fraction drops to 50%. With the strong binding solvent, we observe coherent motion following photodissociation; such motion is absent for argon. One manuscript describing this work is complete, and a second is in preparation. Based upon this work, it was our expectation that strong solvent-solvent interactions would lead to cluster stability. As a further test of this hypothesis, we carried out studies of ICl^- photodissociation in similar cages. The initial studies focused on photodissociation to a state correlating with I^-. To our surprise, we observed production of Cl^- products when the chromophore was only partially solvated. We further expected this electron transfer product to disappear as the cluster size increased. In fact, this electron transfer product became the **only** product when the solvent shell was completed![8] This finding has worrisome implications for the stability of small clusters encapsulating a reactive molecule.

In order to better understand the implications of this result, we have carried out studies of the time dependence of the photofragment yield. For both N_2O and OCS clusters, it appears[1,5,6] that much of the unusual dynamics takes place on an excited state surface. We are working with our colleague Professor R. Parson to better understand the implications of this result. This work has also been summarized in a brief review.[3]

Sanov and Nandi have recently obtained[9,10] product channel-specific two-photon action spectra that allow examination of the caging dynamics in unprecedented detail. The data show that coherent motion of the chromophore cannot be considered separately from dynamics of the cage, and that the evolving solvent configuration favors different types of two-photon products at various stages of evolution. While we employed I_2^- solvated by 11 OCS or 16 CO_2 molecules, the results reflect the general dynamics of caging and will be applicable to other solvated systems.

Direct information about coherent motion of the solvent itself is obtained by following the absorption recovery as detected by specific two-photon products, since it is the instantaneous cage configurations that determine the product branching ratios at given pump-probe delays. For example, the time evolution of the yield ratio of uncaged and caged products, shown in Fig. 1, is independent of the fraction of the initially excited ions that have recombined. Evolution of this ratio directly reflects changes in the solvent configuration. In the statistical, incoherent limit, this ratio should increase monotonically to the observed long delay uncaged/caged ratio, ~ 3. In fact, a very different behavior is observed, indicating that non-statistical dynamics in this 35 atom complex persist for ~ 10 ps. The minimum at 1.8 ps and the maximum at 8 ps correspond to transient cage configurations that favor the production of caged or uncaged two-photon products, respectively. We have interpreted[9] these extremes in terms of the secondary dissociation of the chromophore (by the probe photon) being in-phase or out-of-phase with coherent motion of the cage, respectively.

Since both the solvent cage and the chromophore exhibit coherent motion, we have shown[9] that they can be synchronized to exert control on the two-photon dissociation pathways in cluster ions. For example, the yield of $I_2^-(OCS)_2$ from the two-photon dissociation $I_2^-(OCS)_{11}$ at 790 nm is almost unobservable at long delays; however, substantial dissociation occurs in a narrow delay window coinciding with the characteristic time-scale of $I \cdots I^-$ coherent motion. The determining factor for this channel is a large (impulsive) translational energy release to the solvent at the early stages of evolution, resulting in fast initial relaxation of the cluster. The effectiveness of the energy transfer from photoexcited I_2^- to individual solvent molecules is dependent on the relative phase of the I_2^- and cage motion. The best time for large energy transfer is the same as for enhanced caging: when $I \cdots I^-$ and the solvent cage are out of phase with each other, with the cage moving inwards.

Separately, Mr. Kim employed negative ion photoelectron spectroscopy to obtain detailed knowledge of the binding of small solvent molecules to ionic cores. He has completed a study of the binding of N_2O to OH^- and has obtained binding energies for the first five solvent molecules.[11] The data show clearly that the excess negative charge remains largely localized on the hydroxide moiety. In contrast, when the solvent is ammonia, the photoelectron spectra show clear evidence for electron transfer onto the solvent. As another component of this project, Mr. Kim has used the negative ion photoelectron spectrometer to investigate the electronic structure of several energetic hydrocarbon radicals.[12,13] We have also employed high resolution

autodetachment spectroscopy[14,15] to obtain extremely accurate structures of H_2CCC^- and to probe threshold photodetachment dynamics[16] of OH^-. Collectively, these studies have set the stage for the next level of detailed investigation, where we will observe directly the time dependence of disintegrating cluster ions.

Personnel Supported:

Over the past three years, this award has supported the research of five graduate students in Chemical Physics. These students are Mr. Joseph Kim, Ms. Maria Nadal, Ms. Sreela Nandi, Mr. Todd Sanford and Ms. Tanya Ramond. Dr. Nadal completed her Ph.D. in 1996 and is now a permanently employed at NIST in Gaithersburg, MD. Dr Kim completed his Ph.D. in 1998 and is now employed at Spectralogic Corporation in Boulder. In addition, two outstanding postdoctorals, Dr. Paul Wenthold and Dr. Andrei Sanov. Mr. Kim and Ms. Nandi worked on separate aspects of our studies of the structure and dynamics of ionic clusters, especially issues concerned with the stability of cluster ions and issues concerned with the time dependence of recombination in a size-selected cluster ion. Following the departure of Dr. Nadal, this grant supported the work of Ms. Nandi. Mr. Sanford and Ms. Ramond have been recent (within the past year) additions to the grant, continuing the work on static and dynamical aspects of ionic clusters.

Publications:

1. "Photofragmentation of mass-selected $ICl^-(CO_2)_n$ cluster ions: Solvation effects on the structure and dynamics of the ionic chromophore," *J. Chem. Phys.* **105**, 504-514 (1996) with Maria E. Nadal and Paul D. Kleiber.

2. "Autodetachment dynamics and spectroscopy of vibrationally excited dipole-bound states of H_2CCC^-," *J. Chem. Phys.* **105**, 10706-10718 (1996), with K. Yokoyama, G. W. Leach, J. B. Kim, A. I. Boldyrev and M. Gutowski.

3. "Photoelectron spectroscopy of *m*-xylylene anion," *J. Am. Chem. Soc.* **119**, 1354-1359 (1997), with Paul G. Wenthold and J. B. Kim.

4. "Recombination dynamics of photodissociated I_2^- in size-selected Ar and CO_2 clusters," *J. Chem. Phys.* **106**, 1402-1410 (1997) with V. Vorsa, S. Nandi, P. J. Campagnola and M. Larsson.

5. "High resolution threshold photodetachment spectroscopy of OH^-," *Phys. Rev. A* **55**, 2036-2043 (1997), with Jim R. Smith and Joseph B. Kim.

6. "Femtosecond and Picosecond Dynamics of Ions in Clusters," in *Femtochemistry and Femtobiology: Ultrafast Reaction Dynamics at Atomic-Scale Resolution. Nobel Symposium 101*, Vol. 101 (Imperial College Press, London, 1998), pp. 423-435, with M. E. Nadal, S. Nandi, P. G. Wenthold, J. B. Kim, L. H. Andersen, Y. Ozaki, and D. W. Boo.

7. "An experimental and computational study of the electron affinity of boron oxide," *J. Phys. Chem.* **101**, 4472-4474 (1997), with P. G. Wenthold, J. B. Kim and K. Jonas.

8. "Photoelectron spectroscopy of $OH^-(N_2O)_{n=1-5}$," *J. Chem. Phys.* **108**, 803-837 (1998), with Joseph B. Kim and Paul G. Wenthold.

9. "Transient solvent dynamics and incoherent control of photodissociation pathways in I_2^- cluster ions", *J. Chem. Phys.* **108**, 5155-5158 (1998), with Andrei Sanov and Sreela Nandi.

11. "Incoherent control of photodissociation pathways in I_2^- cluster ions", in Laser Techniques for State-Selected and State-to-State Chemistry, SPIE Proceedings **3271**, p188-193 (1998), with Andrei Sanov.

12. "Photochemistry of $(OCS)_n^-$ cluster ions", *J. Chem. Phys.*, **109**, 1264- 1270 (1998), with Andrei Sanov, Sreela Nandi and Kenneth D. Jordan.

13. "Photodissociation of $I_2^-(OCS)_n$ cluster ions: Structural Implications, J. Phys. Chem., submitted June 1998.

14. "Ultraviolet photoelectron spectroscopy of *o*-, *m*- and *p*- halobenzyl (fluoro, chloro and bromo) anions", *J. Chem. Phys.*, in final preparation, with Joseph Kim and Paul Wenthold.

Interactions/Transitions:

In addition to the publications referenced here, the results of these studies have been presented at a large number of scientific meetings as invited lectures. They have been the subject of posters or lectures at each of the AFOSR Molecular Dynamics Contractors Meetings. The Ph.D. Theses of Drs Kim and Nadal are also publicly available for more detailed information.

In his role as Chair of the National Research Council Commission on Mathematical and Physical Sciences, Dr. Lineberger participates in many activities of AF/DOD relevance. Among these at present are included the Army Research Laboratories Technical Assessment Board, and a Major Materials Facilities Study. Past activities included reviewing next generation naval systems needs for the Naval Studies Board of the NRC.

Inventions and patent disclosures:

There have been no inventions leading to patent disclosures during the period of this grant.

Honors and Awards:

W. C. Lineberger

During the period of this grant:

Awards:

American Academy of Arts and Sciences, 1995
Irving Langmuir Prize in Chemical Physics, American Chemical Society, 1996
Sierra Nevada ACS Section Distinguished Chemist Award, 1997
Georgia Institute of Technology College of Sciences Alumni Achievement Award for Outstanding Contributions to Scholarship and Teaching, 1998

Lectureships:

Spicer Memorial Lecturer, Georgia Institute of Technology, 1995
Bircher Lecturer, Vanderbilt University, 1995
Lord Lecturer, MIT, April, 1996
Centennial Lecturer, University of Texas at Austin, 1997
Stauffer Distinguished Lecturer in Chemistry, University of Southern California, 1997
Sierra Nevada Distinguished Chemist, American Chemical Society, 1997
C. R. Mueller Lecturer, Purdue University, 1998

Major Service Activities:

Chair, Basic Energy Sciences Advisory Committee, Department of Energy, 1993-96
Chair, Topical Group on Laser Science, American Physical Society, 1994-1995
Chair, Section of Chemistry, National Academy of Sciences 1993-1996
Co-Chair, Commission on Physical Sciences, Mathematics and Applications, National Research Council, 1996-1999
Member, Physics Policy Committee, American Physical Society, 1995-present
Chair, NSF Science and Technology Centers Advisory Committee, 1996
Member, Council on Chemical Science, Department of Energy, 1996-1999

Lifetime Prizes/Fellowships:

National Academy of Sciences, 1983
American Physical Society, Fellow
American Association for the Advancement of Science, Fellow
H. P. Broida Prize, American Physical Society, 1980
Bomem-Michelson Prize, Coblentz Society, 1987
William F. Meggers Prize, Optical Society of America, 1988
Phi Beta Kappa National Lecturer, 1989
Earle K. Pyler Prize, American Physical Society, 1992

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1. M. E. Nadal, S. Nandi, D. W. Boo, and W. C. Lineberger, Photodissociation and recombination dynamics of I_2^- in N_2O clusters, J. Chem. Phys. **in preparation,** submitted (1998).
2. V. Vorsa, S. Nandi, P. J. Campagnola, M. Larsson, and W. C. Lineberger, Recombination Dynamics Of Photodissociated I-2(-) In Size-Selected Ar and Co2 Clusters, J. Chem. Phys. **106,** 1402-10 (1997).
3. W. C. Lineberger, M. E. Nadal, S. Nandi, P. G. Wenthold, J. B. Kim, L. H. Andersen, Y. Ozaki, and D. W. Boo, Femtosecond and Picosecond Dynamics of Ions in Clusters in *Femtochemistry and Femtobiology: Ultrafast Reaction Dynamics at Atomic-Scale Resolution. Nobel Symposium 101*, Vol. 101 (Imperial College Press, London, 1998), pp. 423-35.
4. A. M. Sanov, W. C. Lineberger, and K. D. Jordan, **Electronic Structure of (CS2)2-**, Journal of Physical Chemistry A **102,** 2509-11 (1998).
5. A. M. Sanov and W. C. Lineberger, Incoherent control of photodissociation pathways in I2- cluster ions in *SPIE Proceedings*, Vol. 3271, edited by J. W. Hepburn, R. E. Continetti, and M. A. Johnson (SPIE, Bellingham, WA, 1998), pp. 188-95.
6. S. Nandi, A. Sanov, N. Delaney, J. Faeder, and W. C. Lineberger, Photodissociation of I2(-) (OCS)n cluster ions: Structural implications, J. Phys. Chem. **submitted** (1998).
7. A. Sanov, S. Nandi, and W. C. Lineberger, Transient solvent dynamics and incoherent control of photodissociation pathways in I-2(-) cluster ions, J. Chem. Phys. **108,** 5155-8 (1998).
8. M. E. Nadal, P. D. Kleiber, and W. C. Lineberger, Photofragmentation Of Mass-Selected ICl-(CO2)(N) Cluster Ions: Solvation Effects On the Structure and Dynamics Of the Ionic Chromophore, J. Chem. Phys. **105,** 504-14 (1996).
9. A. Sanov, S. Nandi, and W. C. Lineberger, Transient Solvent Dynamics and Incoherent Control of Photodissociation Pathways in I2- Cluster Ions, J. Chem. Phys. **108,** 5155-8 (1998).
10. A. Sanov and W. C. Lineberger, Incoherent Control of Photodissociation Pathways in I2- Cluster Ions, Proc. SPIE **3271,** 188-95 (1998).
11. J. B. Kim, P. G. Wenthold, and W. C. Lineberger, Photoelectron spectroscopy of OH-(N2O)(n=1-5), J. Chem. Phys. **108,** 830-7 (1998).
12. P. G. Wenthold, J. B. Kim, and W. C. Lineberger, Photoelectron-Spectroscopy Of M-Xylylene Anion, J. Am. Chem. Soc. **119,** 1354-9 (1997).
13. P. G. Wenthold, J. B. Kim, K. L. Jonas, and W. C. Lineberger, An Experimental and Computational Study Of the Electron-Affinity Of Boron-Oxide, J. Phys. Chem. **101,** 4472-4 (1997).
14. K. Yokoyama, G. W. Leach, J. B. Kim, and W. C. Lineberger, Autodetachment Spectroscopy and Dynamics Of Dipole Bound-States Of Negative-Ions: 2A1-2B2 Transitions Of H2CCC-, J. Chem. Phys. **105,** 10696-705 (1996).
15. K. Yokoyama, G. W. Leach, J. B. Kim, W. C. Lineberger, A. I. Boldyrev, and M. Gutowski, Autodetachment Spectroscopy and Dynamics Of Vibrationally Excited Dipole-Bound States Of H2CCC-, J. Chem. Phys. **105,** 10706-18 (1996).
16. J. R. Smith, J. B. Kim, and W. C. Lineberger, High-Resolution Threshold Photodetachment Spectroscopy Of OH-, Phys. Rev. A **55,** 2036-43 (1997).